

is rather hinted at than described, I can only conjecture what the substance is ; but I suppose it to be a mixture of the second yellow substance with the products of decomposition of the other three bodies. Green sea-weeds (*Chlorospermeæ*) agree with land-plants, except as to the relative proportion of the substances present ; but in olive-coloured sea-weeds (*Melanospermeæ*) the second green substance is replaced by a third green substance, and the first yellow substance by a third yellow substance, to the presence of which the dull colour of those plants is due. The red colouring-matter of the red sea-weeds (*Rhodospermeæ*), which the plants contain in addition to chlorophyll, is altogether different in its nature from chlorophyll, as is already known, and would appear to be an albuminous substance. I hope, before long, to present to the Royal Society the details of these researches.

“Continuation of an Examination of *Rubia munjista*, the East-Indian Madder, or Munjeet of Commerce.” By JOHN STENHOUSE, LL.D., F.R.S. Received December 21, 1863 *.

In the former, preliminary notice of the examination of the *Rubia munjista* †, the mode of extracting munjistine from munjeet, and a number of its properties, have been already described. I now proceed to detail some results which have been subsequently obtained.

When munjistine is extracted from munjeet by boiling solutions of sulphate of alumina, as the whole of the colouring matter is not extracted by a single treatment with the sulphate of alumina, the operation must be repeated five or six times instead of two or three as was formerly stated. During the boiling of the munjeet with sulphate of alumina, a large quantity of furfural is given off. I may mention, in passing, that the most abundant and economical source of furfural is found in the preparation of garancine by boiling madder with sulphuric acid. If the wooden boilers in which garancine is usually manufactured were fitted with condensers, furfural might be obtained in any quantity without expense.

In addition to the properties of munjistine already described, I may mention that acetate of copper produces in solutions of munjistine a brown precipitate but very slightly soluble in acetic acid.

When bromine-water is added to a strong aqueous solution of munjistine, a pale-coloured flocculent precipitate is immediately produced ; this when collected on a filter, washed and dissolved in hot alcohol, furnishes minute tufts of crystals, evidently a substitution-product. Unfortunately these crystals are contaminated by a resinous matter, from which I have been unable to free them, and therefore to determine their composition.

When munjistine is strongly heated on platinum-foil, it readily inflames and leaves no residue ; when it is carefully heated in a tube, it fuses, and crystallizes again on cooling. If heated very slowly in a Mohr's apparatus,

* Read January 14. See Abstract, page 86.

† Proceedings, vol. xii. p. 633.

munjistine sublimes in golden scales and broad flat needles of great beauty; these have all the physical characters and the same composition as the original substance. If the sublimation be continued for a long time at the lowest possible temperature consistent with its volatilization, the whole of it is obtained with scarcely any loss.

The following are the results of the ultimate analysis of different samples of munjistine:—

I. ·314 grm. of munjistine yielded ·732 grm. carbonic acid and ·106 grm. of water.

II. ·228 grm. of munjistine yielded ·535 grm. carbonic acid and ·0765 grm. water.

III. ·332 grm. of munjistine yielded ·7795 grm. of carbonic acid and ·1125 grm. of water.

IV. ·313 grm. of munjistine yielded ·734 grm. of carbonic acid and ·1095 grm. of water.

	Theory.	I.	II.	III.	IV.
C ₁₆ =96	64·00	63·60	64·00	64·04	63·97
H ₆ = 6	4·00	3·77	3·73	3·76	3·89
O ₆ =48	32·00	32·63	32·27	32·20	32·14

The carbon in No. I. is rather lower than that of the other three; this is owing to the specimen not being quite free from alumina; moreover it was burnt with oxide of copper, the others with chromate of lead. No. III. is the sublimed munjistine. All the analyses were made on specimens prepared at different times.

Lead Compound.

When aqueous or alcoholic solutions of munjistine and acetate of lead are mixed, a flocculent precipitate of a deep orange-colour falls, which changes to scarlet on the addition of a slight excess of acetate. The best method of preparing it is to dissolve munjistine in hot spirit and add to the filtered solution a quantity of acetate of lead insufficient to precipitate the whole of the munjistine, then to wash thoroughly with spirit, in which the lead compound is but slightly soluble, and dry first *in vacuo*, and then in the water-bath.

- I. ·836 grm. lead compound gave ·407 grm. oxide of lead.
- II. ·625 grm. lead compound gave ·302 grm. oxide of lead.
- III. ·428 grm. lead compound gave ·2075 grm. oxide of lead.
- IV. ·523 grm. lead compound gave ·253 grm. oxide of lead.
- V. ·2705 grm. lead compound gave ·3445 grm. of carbonic acid and ·0445 grm. water.
- VI. ·5350 grm. lead compound gave ·6830 grm. carbonic acid and ·0920 grm. water.

	Theory.	I.	II.	III.	IV.	V.	VI.
C ₅₀ = 486	34·93	34·73	34·82
H ₂₅ = 25	1·82	1·83	1·91
O ₂₅ = 200	14·55
6PbO	669·6	48·70	48·70	48·32	48·50	48·38

All the specimens were prepared at different times, except IV. and V., which are analyses of the same specimen. The lead compound therefore seems to approach nearly to the somewhat anomalous formula $5(C_{16}H_6O_5) + 6PbO$, being a basic lead-salt; it is, however, perfectly analogous to the lead compound of purpurine, $5(C_{18}H_6O_5) + 6PbO$, described by Wolff and Strecker*.

From these analyses of the lead compound and also from the ultimate analyses of munjistine itself, it is pretty evident that its true formula is $C_{16}H_6O_6$.

Neither sublimed munjistine nor that obtained by crystallization from alcohol, when dried at the ordinary temperature *in vacuo*, loses weight at 110°C . It is not improbable, however, that the gelatinous uncrystallizable precipitate, which separates on the cooling of boiling saturated aqueous solutions of munjistine, is a hydrate.

From some experiments made on a considerable scale, I find that ordinary madder does not contain any munjistine. In order to ascertain this fact, a considerable quantity of garancine from Naples Roots, and likewise some which had been subjected to the action of high-pressure steam according to Pincoff and Schunck's process, were treated with boiling bisulphide of carbon, and the product obtained on evaporating the bisulphide repeatedly extracted with large quantities of boiling water; the solution, when acidulated with sulphuric acid, gave an orange-red precipitate from which I was unable to obtain any munjistine. Professor Stokes succeeded, however, in detecting the presence of alizarine, purpurine, and rubiacine in it †.

The production of phthalic acid from alizarine, purpurine, and munjistine, together with a comparison of their subjoined formulæ, indicates the very close relationship between these three substances, the only true colouring principles of the different species of madder with which we are acquainted.

Alizarine	$C_{20}H_6O_6$,
Purpurine	$C_{18}H_6O_6$,
Munjistine	$C_{16}H_6O_6$.

Two other very convenient sources of phthalic acid are—first, the dark red resinous matter, combined with alumina, which is left undissolved by the bisulphide of carbon in the preparation of munjistine; secondly, the large quantity of green-coloured resinous matter which remains behind after extracting the alizarine from Professor Kopp's so-called "green alizarine" by means of bisulphide of carbon. I have repeated Marignac's and Schunck's experiments of distilling a mixture of phthalic acid and lime; and, like both of these chemists, I observed a quantity of very aromatic benzol to be produced, which, by the action of strong nitric acid, readily yielded nitrobenzol, and from this, by the action of reducing agents, aniline. The only impurity in the benzol from phthalic acid appears to be a minute

* Annalen der Chemie, lxxv. p. 24.

† He has since informed me that he has succeeded in demonstrating the absence of munjistine.

quantity of an oil, having an aromatic odour, resembling that produced from cinnamic acid by the action of hypochlorite of lime.

Tinctorial power of Munjistine and Munjeet.

Prof. Runge stated, in 1835, that munjeet contains twice as much available colouring matter as the best Avignon madder. This result was so unexpected, that the Prussian Society for the Encouragement of Manufactures, to whom Professor Runge's memoir was originally addressed, referred the matter to three eminent German dyers, Messrs. Dannenberger, Böhm, and Nobiling. These gentlemen reported, as the result of numerous and carefully conducted experiments, that so far from munjeet being richer in colouring-matter than ordinary madder, it contained considerably less. This conclusion has been confirmed by the experience of my friend Mr. John Thom, of Birkacre, near Chorley, one of the most skilful of the Lancashire printers.

From a numerous series of experiments I have just completed, I find that the garancine from munjeet has about half the tinctorial power of the garancine made from the best madder, viz. Naples Roots. These, however, yield only about 30 to 33 per cent. of garancine, while munjeet, according to my friend Mr. Higgin, of Manchester, yields from 52 to 55 per cent. Taking the present prices therefore of madder at 36 shillings per cwt., and munjeet at 30 shillings, it will be found that there will be scarcely any pecuniary advantage in using munjeet for ordinary madder-dyeing. The colours from munjeet are certainly brighter, but not so durable as those from madder, owing to the substitution of purpurine for alizarine. There is, however, great reason to believe that some of the Turkey-red dyers are employing garancine from munjeet to a considerable extent. When this is the case they evidently sacrifice fastness to brilliancy of colour. By treating such a garancine with boiling water, and precipitating by an acid in the way already described, its sophistication with munjeet may very readily be detected. The actual amount of colouring matter in munjeet and the best madder is very nearly the same; but the inferiority of munjeet as a dye-stuff results from its containing only the comparatively feeble colouring matters, purpurine and munjistine, only a small portion of the latter being useful, whilst the presence of munjistine in large quantity appears to be positively injurious. So much is this the case, that when the greater part of the munjistine is removed from munjeet-garancine by boiling water, it yields much richer shades with alumina mordants than before.

PURPUREINE.

Action of Ammonia on Purpurine.

When purpurine is dissolved in dilute ammonia and exposed to the air in a vessel with a wide mouth in a warm place for about a month, ammonia and water being added from time to time as they evaporate, the purpurine almost entirely disappears, whilst a new colouring-matter is formed which dyes unmordanted silk and wool of a fine rose-colour, but is incapable of

dyeing vegetable fabrics mordanted with alumina. If, however, strong ammonia be employed to dissolve the purpurine, considerable heat is produced—a rise of temperature of as much as 20° C. taking place if the bulb of a thermometer be immersed in finely divided purpurine and strong ammonia poured on it.

The purpurine employed in these experiments was prepared by Kopp's process, and I am indebted for it to my friend Professor Crace Calvert.

The solution of the new substance, *purpureine*, is filtered to separate dust, &c., as well as a black substance insoluble in dilute ammonia; it is then added to a considerable quantity of dilute sulphuric acid, boiled for a short time, and allowed to cool. When cold, the impure purpureine is collected on a filter, well washed, and dissolved in a small quantity of hot alcohol. The spirituous solution is again filtered into a quantity of very dilute boiling sulphuric acid, about 1 part acid to from 50 to 100 of water; when cold, the precipitate is collected and again well washed; A crystallization out of boiling very dilute acid now renders it quite pure. This somewhat long and tedious process is necessary to free it from an uncrystallizable black substance, a part of which is separated when the crude purpureine is dissolved in alcohol, and a part is left behind at the last crystallization.

This compound being in its mode of formation and physical properties very analogous to orceine, I have called it purpureine. When crystallized by the spontaneous evaporation of its alcoholic solution, or from boiling dilute sulphuric acid under peculiar conditions of aggregation, it presents a fine iridescent green colour by reflected light; whilst under the microscope it appears as fine long needles of a very deep crimson colour. As obtained by the process above described, it has, however, but little of the iridescent appearance, being of a brownish-red colour with a faint tinge of green. It is almost insoluble in cold dilute acids, and is in great part precipitated from its aqueous solution by common salt, thus greatly resembling orceine. It is almost insoluble in bisulphide of carbon, very slightly so both in ether and in cold water, much more so in hot, and very soluble in spirit both hot and cold and in water rendered slightly alkaline. It is readily soluble in *cold* concentrated sulphuric acid, and is precipitated unaltered by water; on heating, however, it is destroyed.

Its aqueous solution gives a deep-red precipitate with chloride of zinc; with chloride of mercury a purple gelatinous precipitate; and with nitrate of silver a precipitate of a very dark brown colour slightly soluble in ammonia. I have been favoured with the following optical examination by Professor Stokes:—

“ Its solutions show bands of absorption just like purpurine in *character*, but in some cases *considerably different in position*. The etherial and acidulated (acetic acid) alcoholic solutions show this strongly. The tint is so different in purpurine and its derivative, that the intimate connexion revealed by the prism would be lost by the eye. A drawing of the spectrum for purpurine would serve for its derivative (purpureine), if the bands were simply pushed a good deal nearer the red end.”

I. ·3435 grm. pupureine gave ·8230 grm. carbonic acid and ·1240 grm. of water.

II. ·340 grm. purpureine gave ·813 grm. carbonic acid and ·123 grm. of water.

III. ·336 grm. purpureine gave ·01552 grm. nitrogen.

IV. ·535 grm. purpureine gave ·02453 grm. nitrogen.

	Theory.	I.	II.	III.	IV.
C ₆₆ =	396	65·13	65·36	65·22
H ₂₄ =	24	3·95	4·01	4·02
N ₂ =	28	4·60	4·62
O ₂₀ =	160	26·32	4·58
	608	100·00		

The formula therefore appears to be C₆₆ H₂₄ N₂ O₂₀?

Nitropurpureine.

When purpureine is dissolved in a small quantity of moderately strong nitric acid, spec. grav. about 1·35, and heated to 100° C., it gives off red fumes, and on being allowed to cool, a substance separates in magnificent scarlet prisms somewhat like chromate of silver, only of a brighter colour; it is quite insoluble in water, ether, and bisulphide of carbon, and very slightly soluble in spirit, but soluble in hot moderately strong nitric acid, from which it separates on standing for a considerable time. If boiled with strong nitric acid, it is slowly decomposed. When heated, it deflagrates: from this circumstance, and considering its mode of formation, it is evidently a nitro-substitution compound; I have therefore called it nitropurpureine.

Owing to the small quantity which I have hitherto been able to procure, I have not yet determined the composition of this beautiful body, which is finer in appearance than any of the derivatives from madder I have as yet met with.

Action of Ammonia on Alizarine.

The alizarine which was employed for the subjoined experiments was obtained by extracting Professor E. Kopp's so-called green alizarine* with bisulphide of carbon. It yields only about 15 per cent. of orange-red alizarine. This was crystallized three times out of spirit, from which it usually separates as a deep-orange-coloured crystalline powder. Unfortunately this alizarine still contains a quantity of purpurine, from which it is impossible to purify it either by crystallization or sublimation. Accordingly, when treated with ammonia by the method already described for purpurine, while it yields a substance analogous to *purpureine*, the product is impure, being contaminated with purpureine. This mixture has been examined by my friend Professor Stokes, who finds that it contains purpureine, derived from the purpurine present as an impurity in the alizarine employed, and another substance very like alizarine in its optical properties, probably a new substance (*alizareine*), bearing the same relation to alizarine that

* I am also indebted to Professor Calvert for the "green alizarine."

purpureine does to purpurine*. The following is an extract from a letter I received from Professor Stokes :—

" It would be very unlikely *à priori* that such a simple process as that of Kopp should effect a perfect separation of two such similar bodies as alizarine and purpurine ; and as I find his purpurine is free from alizarine, it would be almost certain *à priori* that his 'green alizarine' would contain purpurine, and the two would be dissolved by bisulphide of carbon, and might very well afterwards be associated by being deposited in intermingled crystals, if not actually crystallizing together."

Action of Ammonia on Munjistine.

This reaction with munjistine was only tried on a very small scale, but the results were by no means satisfactory. The munjistine was completely destroyed, the greater part being changed into a brown humus-like substance, insoluble in ammonia,—the remainder forming a colouring-substance, analogous to purpureine, but not crystalline. It dyed unmordanted silk a brownish-orange colour.

The combined action of ammonia and oxygen, therefore, on the three colouring-substances alizarine, purpurine, and munjistine, is to change them from adjective to substantive dye-stuffs. I think it not improbable that if this archilizing process were applied to various other colouring matters, they would be found capable of undergoing similar transformations.

Action of Bromine on Alizarine.

A boiling saturated solution of alizarine in alcohol is mixed with about six or eight parts of distilled water, and to this when cold about one or one and a half parts of bromine water are added, when a bright yellow amorphous precipitate is produced. After standing twelve or sixteen hours, the solution is filtered ; and if the clear filtrate be now carefully heated so as to expel the spirit, a substance of a deep orange-colour is deposited, consisting of very fine needles, which are contaminated with a small quantity of resin if a great excess of bromine has been employed. These needles are soluble in spirit and ether, insoluble in water, and soluble in bisulphide of carbon, from which they crystallize by spontaneous evaporation, in dark-brown nodules. With soda they give the same purple colour as alizarine. They dye cloth mordanted with alumina a dingy brownish red, very different from the colour produced by ordinary crystallized alizarine. The following optical examination is from a letter of Professor Stokes :—

"Bromine Derivative of Alizarine."

" I can hardly distinguish this substance from alizarine. The solutions

* Since this paper was communicated to the Royal Society, I find by a notice in Kopp and Wills's 'Jahresbericht' for 1862, p. 496, that a similar experiment upon alizarine had been made by Schützenberger and A. Paraf. The product of one preparation which they obtained, and to which they have given the name of *alizarinamid*, yielded a formula $C_{40}H_{15}NO_{12}$, and another preparation gave the formula $C_{80}H_{48}N_2O_{24}$, both being, when dry, nearly *black amorphous* substances. It appears, therefore, from the results of MM. Schützenberger and Paraf's experiments, that these gentlemen were not more successful in obtaining a pure product from the action of ammonia on alizarine than I have been.

in alcohol containing potassa show three bands of absorption just alike in appearance. By measurement it seemed probable that the bromine substance gave the bands a *little* nearer to the red end; but the difference, if real, was very minute. The fluorescent light of the ethereal solution was, I think, a trifle yellower in the bromine substance, that of alizarine being more orange."

The following are the results of the ultimate analysis of the brominated alizarine dried at 100° C. :—

- I. ·375 grm. of substance gave ·207 grm. bromide of silver.
- II. ·703 grm. of substance gave ·389 grm. bromide of silver.
- III. ·401 grm. of substance gave ·221 grm. bromide of silver.
- IV. ·543 grm. of substance gave ·300 grm. bromide of silver.
- V. ·3575 grm. of substance gave ·695 grm. of carbonic acid and ·0760 grm. of water.
- VI. ·454 grm. of substance gave ·8790 grm. of carbonic acid and ·0965 grm. of water.

	Theory.	I.	II.	III.	IV.	V.	VI.
C ₆₀	= 360	52·94	53·03	52·81
H ₁₆	= 16	2·35	2·36	2·36
Br ₂	= 160	23·53	23·49	23·54	23·45	23·51
O ₁₈	= 144	21·18
		680	100·00				

From this somewhat anomalous formula,



I was for some time inclined to think that it might be a mixture of brominated alizarine with free alizarine; but as all the six samples analyzed were prepared at different times, it is highly improbable that such uniform analytical results could be obtained if they were from a mere admixture of substances. The existence of a brominated compound is also confirmed by its dyeing properties, which differ so remarkably from those of alizarine.

Action of Bromine on Purpurine.

When pure purpurine is dissolved in spirit mixed with a considerable quantity of water, and an aqueous solution of bromine added, as in the case of alizarine, a yellow amorphous precipitate is produced. The solution separated from this by filtration, when heated to expel the spirit, gives *no precipitate whilst hot*; but on cooling, a very small quantity of a brown resinous powder is deposited. From this it is evident that the presence of a small quantity of purpurine in alizarine will not interfere with the production of pure brominated alizarine, if the precaution be taken to collect it from the solution whilst it is still hot.

I think it right to state that the experiments and analyses detailed in the preceding paper have been performed by my assistant, Mr. Charles Edward Groves. I cannot conclude this paper without again acknowledging the essential services I have received from Professor Stokes, who kindly submitted the different products obtained by me to optical examination.